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(54) **Alcohol control of lightly crosslinked foamed polymer production.**

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Description

This invention relates to a process for preparing lightly crosslinked, extruded, closed-cell foamed polymer articles. It particularly pertains to a process using expandable ethylenic or styrenic polymer
5 compositions containing a reversible crosslinking system which permits alcohol control of the degree of crosslinking of the polymer prior to extrusion foaming.

It is well known to make closed-cell polymer resin foams by the process of extrusion foaming wherein a normally solid thermoplastic polymer resin is heat-plastified and mixed under pressure with a volatile material to form a flowable gel which is then passed through a shaping orifice or die opening into a zone of
10 lower pressure. Upon the release of pressure, the volatile constituent of the gel vaporizes, forming a gas phase cellular structure in the gel which cools to a corresponding cellular foamed solid resin. Desirably, the resulting gas cells are substantially uniform in size, uniformly distributed through the foam body, and closed, i.e., separated from each other by membrane walls of resin.

It is also known that the use of relatively lightly to moderately crosslinked polymers generally improves
15 the quality of foamed polymer articles.

In addition, lightly crosslinking in some instances make possible foaming of polymer foams which otherwise cannot easily be produced. Some polymers such as linear polyethylenes are difficult to foam by extrusion. It is generally believed that poor melt strength together with a sharp change in melt viscosity near the transition temperature makes extrusion foaming of linear polyolefins difficult. Since light crosslinking
20 increases polymer viscosity and thus broadens the range of foaming temperature, crosslinking would also be desirable from this standpoint.

However, a crosslinked polymer is difficult to extrude. As such, past practices have ordinarily not involved crosslinking during normal thermoplastic fabrication processing procedures such as production of extruded foamed polymer articles. As a result, most research works have been directed to production of a
25 crosslinked polymer composition expandable during post-extrusion secondary foaming. Recently, however, advances have been made in overcoming some of the problems involved.

For example, Corbett's U.S. Patent No. 4,454,086 (assigned to the assignee of the present invention) discloses making crosslinked styrene polymer foams by an extrusion process. In Corbett a styrene/acrylic acid copolymer is lightly crosslinked in the foam extrusion line with a multi-functional epoxy resin. Since
30 covalent bonds formed by the acid/epoxy reactions are not reversible, the scheme calls for a close control of epoxy level or the reaction rate.

In addition, silane and peroxide crosslinkers have been used to crosslink polyolefin and polystyrene foams which may be produced by using an extrusion foaming machine. U.S. Patents 4,446,254; 4,421,867; 4,351,910, and 4,252,906, amongst others, fall into this category. Sugitani Patent No. 4,351,910, for
35 example, proposes improving the heat resistance of a polystyrene foam by introducing an organosilane compound into a styrene series resin. The silane structure is chemically bonded to the molecular structure of the styrene series resin by addition polymerization, by graft polymerization or by free radicals. The degree of crosslinking is disclosed as being temperature dependent. As such, Sugitani states that crosslinking can be delayed by low temperature processing since it only proceeds gradually at tempera-
40 tures below 100° C.

It is also known that crosslinking can be delayed by swelling the polymer so as to permit working in crosslinking agents at temperatures below the starting point of the used crosslinking agents. Thus, Slogburg's Patent No. 3,452,123 discloses adding an organic solvent to swell an ethylene polymer and then admixing therein, at a temperature below the starting point of the used crosslinking agent, the propellant
45 and the crosslinking agent. Extrusion of the resulting mass is carried out at temperatures above the softening point of the swelled compound. This system is said to result in delay of the crosslinking so that it, preferably, occurs in the extrusion die.

Still, the delayed crosslinking system of Slogburg, like the crosslinking and foaming systems of the others mentioned, is not reversible and therefore requires rather careful temperature and processing
50 controls. The need exists therefore for improved means for controlling the degree of crosslinking of an expandable polymer prior to extrusion foaming.

The present invention meets that need by use of a reversible gas-yielding crosslinking reaction which is delayed in the foam extrusion line in the presence of gaseous products (alcohols) but proceeds further during foam expansion at the die. Thus, the crosslinking control of the present invention is primarily
55 accomplished by inclusion of an aliphatic alcohol, along with the blowing agent, in the polymer admixture.

The present invention is a process for preparing lightly crosslinked olefin or styrenic polymer foamed articles having a closed-cell structure, characterized by the steps of:

a) providing an olefin or styrene polymer material, selected from the group consisting of:

(1) olefin copolymers;

(2) styrene copolymers, vinyltoluene polymers, styrene/acrylonitrile/hydroxy ethylacrylate terpolymers and mixtures thereof; and

(3) a polymer of styrene having hydroxyl, carboxylic acid and carbonyl functional groups, optionally mixed with anyone of the foregoing styrenic polymers.

b) admixing said olefin or styrene polymer material with (1) a blowing agent, (2) a crosslinking agent selected from the group consisting of silane, azido silane, titanate and amino compounds which upon reaction with said olefin or styrene polymer material reversibly releases alcohol, and (3) additionally admixing a sufficient amount of alcohol to control the degree of crosslinking of said olefin or styrene polymer material in the admixture which is thereby formed, and

c) extruding said admixture and activating said blowing agent in such a manner as to expand said olefin or styrene polymer material to a cellular structure and at the same time dissipate said alcohol, whereby foaming and crosslinking of said olefin or styrene polymer material concurrently takes place.

Since a delayed crosslinking system makes control of crosslinking easier, this permits, for example, a high level of crosslinking with the extrusion foaming process. Increased heat distortion temperatures are the benefits of such a highly crosslinked polymer.

Another advantage of the presence of alcohol in the blowing agent is that it can accelerate steam expansion by lowering the glass transition temperature of the polymer and also by promoting water vapor transmission. Faster permeation of water could result from its enhanced solubility in the polymer/alcohol phase and its higher diffusivity in the alcohol-plasticized polymer. On-line steam expansion, in turn, drops foam density enabling production of highly expanded polymer foams.

Basically, the foam extrusion process relies on physical equilibrium between a polymer and blowing agent. A physical blowing agent is mixed in and equilibriated with the polymer in the foam extrusion line. The blowing agent remains dissolved and contained in the polymer phase. Upon exposure to atmospheric pressure at the exit of the die, the gel undergoes phase separation. The blowing agent separates from the polymer phase and rapidly diffuses into the microcavities expanding the polymer to a cellular structure.

A gas-yielding reversible reaction can reach a chemical equilibrium in the foam extrusion line much the same way as the physical equilibrium between polymer and blowing agent. The crosslinking reaction of the present invention is, thus, one which reversibly produces a gaseous alcohol reaction product. In the foam extrusion line, the gaseous product remains dissolved in the polymer, limiting formation of cross-bonds to an equilibrium level. At the die during foam expansion, the volatile product rapidly diffuses into the cell cavities depleting its concentration in the polymer phase and letting the reaction proceed further. The in situ formed additional cross-bonds help set the expanding bubbles.

For successful implementation of this mechanism:

1) the crosslinking reaction must be reversible yielding a gaseous product and

2) the gaseous product must possess the properties required for a good secondary blowing agent; (a) adequate solubility in the polymer in the line, (b) high diffusivity during foam expansion, (c) low solubility at ambient temperature, and (d) low toxicity and flammability.

It has been found that various crosslinking reaction systems which reversibly yield an alcohol may be used since many alcohols possess the required secondary blowing agent characteristics. Crosslinking agents which do so with ethylenic and styrenic polymers are silanes, azido silanes, titanates and amino compounds.

Generally, any grafted silane having more than one hydrolyzable group is useful as the crosslinking agent. The silane may be an organofunctional silane of the general formula R R′ Si Y$_2$ in which R represents a vinyl, epoxy or amine functional radical attached to silicon through a silicon carbon bond and composed of carbon, hydrogen and optionally oxygen or nitrogen, each Y represents a hydrolyzable organic radical and R′ represents a hydrocarbon radical or Y. Examples of such organofunctional silanes are found in U.S. Patent No. 3,646,155. Alternatively, the silane may be an alkoxy silane of the general formula R$_a$Si-(OR′)$_b$,where "a" is 1,2 and "b" is 2,3, R is methyl or organoreactive alkyl group and OR′ is a hydrolyzable alkoxy group, or it may be a hydroxy functional silicone intermediate. Examples of such alkoxy silanes are found in U.S. Patent No. 4,351,910.

The silane crosslinking agent is preferably one which is both organofunctional and alkoxy. Examples of organofunctional alkoxy silanes which may be used are gamma-glycidoxypropyltrimethoxy silane, gamma-methacryloxypropyltrimethoxy silane, vinyltrimethoxy silane, vinyltriethoxy silane, N-(2-aminoethyl)-3-aminopropyltrimethoxy silane, N-β-(N-vinyl benzyl amino) ethylaminopropyltrimethoxy silane, methyl-trimethoxy silane, and gamma -aminopropyl triethoxy silane.

While all of the crosslinking agents utilized in the present invention are useful for producing lightly crosslinked polymer foams, the most preferred crosslinking agents are the azido functional silanes of the

general formula R R'SiY$_2$, in which R represents an azido functional radical attached to silicon through a *silicon to carbon bond and composed of carbon, hydrogen, optionally sulfur, nitrogen, and oxygen, each Y represents a hydrolyzable organic radical, and R' represents a monovalent hydrocarbon radical or a hydrolyzable organic radical. Examples of the azido functional silanes which may be used are found in U.S.*

5 Patents 3,705,911 and 4,401,598. Preferred amongst the azido functional silanes are 2-(trimethoxysilyl) ethyl phenyl sulfonyl azide and (triethoxy silyl) hexyl sulfonyl azide.

The titanate crosslinking agent may be a titanium alkoxide of the general formula Ti(OR)$_4$ where R is C$_1$, to C$_{18}$ alkyl or it may be a titanate coupling agent of the general formula (RO)$_m$ - Ti (O - X - R^2 - Y)$_n$ wherein R is typically alkyl, X is carboxyl, R^2 is an alkyl carbon chain, Y is reactive double bond or amino,

10 and m and n are integers which total 4. Preferred amongst the titanates are titanium isopropoxide, and tetramethyl titanate.

Preferred as amino crosslinking agents are hexamethoxymethylmelamine (HMMM) and alkylated glycoluriIformaldehyde resins.

The olefinic copolymer may be an alpha-olefin polymer with an α,β ethylenically unsaturated carboxylic

15 acid, hydroxyl ethyl acrylate or carbon monoxide. The styrenic polymer material may be a styrene copolymer, a styrene polymer having hydroxyl, carboxylic acid and carbonyl functional groups, a vinyl toluene polymer, or mixtures thereof. For example, the ethylenic or styrenic copolymer may be styrene/acrylic acid copolymers, ethylene/acrylic acid copolymers, styrene/acrylonitrile/hydroxy ethyl-acrylate terpolymers, and mixtures thereof.

20 The blowing agent may be selected from conventional physical blowing agents such a chlorofluorocarbons, chlorocarbons, hydrocarbons and alcohols. Preferred are dichlorodifluoromethane, trichloromonofluoromethane, dichlorotetrafluoroethane, and mixtures thereof.

When halogenated hydrocarbon compounds are used as the blowing agent, there can be from about 0.013 to about 0.50 gram mole, and preferably 0.040 to 0.30 gram mole of such blowing agent per 100

25 grams of polymer resin in the admixture.

The alcohol used to control the degree of crosslinking is preferably an aliphatic alcohol such as methanol (methyl alcohol), ethanol (ethyl alcohol), n-propanol (propyl alcohol), i-propanol (isopropyl alcohol) and butanols (butyl alcohols).

Preferably, the alcohol is added during processing along with the blowing agent. For example, an 80/20

30 mixture of dichlorodifluoromethane/methanol may be used as the blowing agent/alcohol. The weight ratio of blowing agent to alcohol may, however, vary from approximately 70/30 to 95/5.

In some instances, however, an alcohol can serve the dual purpose of crosslinking delaying and blowing agent when used with a crosslinking agent in accordance with the present invention. Alcohols are somewhat deficient in blowing power with their low vapor pressure and high solubilities in certain polymers. Lightly

35 crosslinking permits raising the foaming temperature and thus the blowing efficiency leading to low foam densities. Thus, it is possible to use alcohol alone as the blowing agent/crosslinking control with certain crosslinking agents and polymers.

In any event, addition of an alcohol along with the blowing agent permit control of the degree of crosslinking when the crosslinking reaction mechanism is a reversible one yielding alcohols.

40 For example, the fundamental chemistry involved in silane crosslinking is depicted by the following reactions:

45 $$\equiv Si-OCH_3 + H_2O \quad \rightleftharpoons \quad \equiv Si-OH + CH_3OH\uparrow \qquad (a)$$

$$\equiv Si-OH + HO-Si\leq \quad \rightleftharpoons \quad \equiv Si-O-Si\leq \; + H_2O \qquad (b)$$

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$$2 \equiv Si-OCH_3 + H_2O \quad \rightleftharpoons \quad \equiv Si-O-Si\leq \; + 2CH_3OH\uparrow \qquad (c)$$
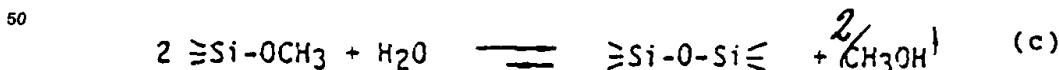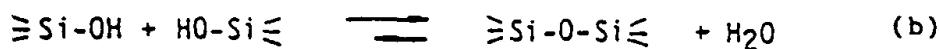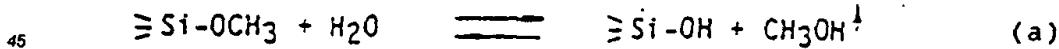
55 Methoxy silane hydrolyzes reversibly to silanol releasing methanol by reaction (a). Silanols condense to siloxane linkages releasing water by reaction (b). Overall two moles of methoxy silane and one mole of water reversibly produce one mole of siloxane crosslink releasing two moles of methanol by reaction (c).

Alkoxy functional silanes graft on ethylenic or styrenic polymers having carboxylic acid groups through reaction of carboxylic acids with methoxy groups forming acyloxy silane linkages, again with the release of alcohol.

Amino functional silanes graft on polymers having carboxylic acid or anhydride groups. Silanes having
5 epoxy functional groups also react with carboxylic acid-functional polymers such as copolymers of acrylic acid with ethylene or styrene. Since reversible, alcohol yielding, reaction mechanisms occur with silanes of this type, these crosslinking mechanisms are controllable by use of an alcohol in the processing.

A titanium alkoxide reversibly reacts with a carboxylic acid or hydroxyl functional polymer releasing alcohols. Amino crosslinking agents can also be used to crosslink polymers containing hydroxyl, carboxy or
10 amide functionality. Amino crosslinking agents crosslink such functionalized polymers through a condensation reaction releasing alcohol as a product. In addition, titanate and amino crosslinking agents are inexpensive permitting a high level of use without cost penalties.

However, as noted, the silane, titanate and amino crosslinking mechanisms require a polymer having a functional group such as carboxylic acids. An azido functional silane is unique in that it can graft on most
15 polymers through the nitrine insertion reaction:

$$N_3SO_2 \text{---} \langle O \rangle \text{---} CH_2CH_2Si(OCH_3)_3 \longrightarrow N_2 + :NSO_2 \langle O \rangle \text{---} CH_2CH_2Si(OCH_3)_3$$
$$\underline{I}$$

$$\geq C - H + \underline{I} \longrightarrow \geq C - \overset{\overset{\displaystyle H}{\displaystyle |}}{N} - SO_2 \langle O \rangle \text{---} CH_2CH_2Si(OCH_3)_3$$
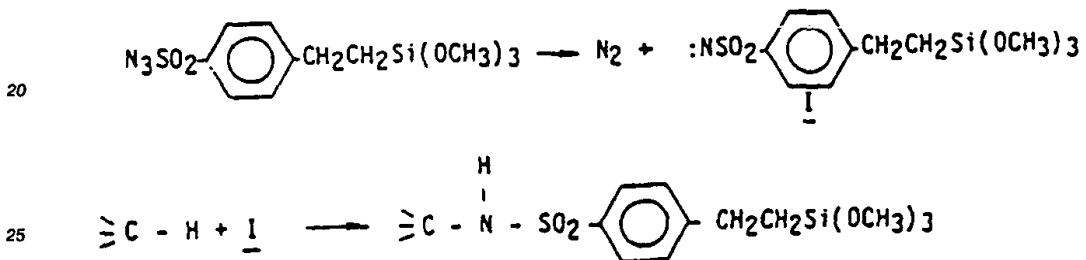
Therefore, an azido functional silane can graft on and crosslink polyethylene and polystyrene having no reactive functional group.
30 Accordingly, azido functional silanes are the preferred crosslinking agent and will be used as the illustrative crosslinking agent in the general description of the preferred embodiment which follows. Still, as long as the reaction between the polymer and the crosslinking agent is a reversible one yielding alcohols, it is controllable in accordance with the instant invention, and various of the following examples illustrates use of others of the crosslinking agents.

35 In accordance with the process of the present invention, lightly crosslinked polymer foams may be made on conventional melt processing apparatus such as by continuous extrusion from a screw-type extruder. Such an extruder typically comprises a series of sequential zones including a feed zone, compression and melt zone, metering zone, and mixing zone. The barrel of the extruder may be provided with conventional electric heaters for zoned temperature control.

40 An inlet, such as an injection nozzle, is provided for adding a mixture of fluid blowing agent and crosslinking agent under pressure to the polymer in the extruder barrel between the metering and mixing zones. Crosslinking agent is pumped, in a controllable manner, into the stream of fluid blowing agent upstream of the injection nozzle. The blowing agent and crosslinking agent are compounded into the starting polymer in a conventional manner to form a flowable gel or admixture, preferably in a continuous
45 manner. Thus, the polymer, blowing agent, and crosslinking agent may be combined in the mixing zone of an extruder using heat to plastify the polymer resin, pressure to maintain the blowing agent in a liquid state, and mechanical working to obtain thorough mixing.

The blowing agent is compounded into the flowable gel in proportions to make the desired degree of expansion in the resulting foamed cellular product to make products having foamed densities down to about
50 9.6 kg m^{-3} (0.6 pcf). Depending on the amount of blowing agent added, the resulting foamed materials may have densities from about 9.6 to 240.3 kg m^{-3} (0.6 to 15.0 pcf).

The alcohol for crosslinking control purposes is preferably added with the blowing agent. As mentioned, the blowing agent/alcohol ratio, by weight, may vary from approximately 70/30 to 95/5.

Since the condensation reaction of silanols to siloxanes is catalyzed by the presence of certain metal
55 catalysts such as dibutyl tin dilaurate or butyl tin maleate, it is preferred that when azido silanes are used as the crosslinking agent in the present invention, that a small amount of such catalyst also be added to the polymer melt.

The crosslinking reaction is self-controlled in the extruder by the presence of the gaseous reaction product, namely an alcohol, which limits the reaction. However, the crosslinking reaction proceeds during foam expansion at the exit of the die as the alcohol diffuses into the gaseous phase with the volatile blowing agent.

5 In this manner, crosslinking of the polymer gel in the extruder is controlled so that the gel remains flowable until it exits the die to a zone of lower pressure. There, the crosslinking reaction proceeds, which stabilizes gas bubble and cell formation as the olefinic polymer is expanded. Because the degree of crosslinking in the extruder can be controlled, a greater proportion of azido silane crosslinking agent may be added and, a higher degree of crosslinking in resultant polymer foam may be obtained.

10 Suitable azido-functional silane compounds includes the group of azido trialkoxysilanes such as 2-(trimethoxysilyl) ethyl phenyl sulfonyl azide (commercially available from Petrarch Systems, Inc., Bristol, Pennsylvania) and (triethoxy silyl) hexyl sulfonyl azide (commercially available as Azcup D-98® from Hercules, Inc., Wilmington, Del.). The azido functional silane crosslinking agent is added in an amount between about 0.01 to 2.0 parts per hundred (pph), by weight, of ethylenic or styrenic polymer. An 15 especially preferred range of addition is between 0.02 to 1.0 pph of azido silane crosslinking agent.

The discharge end of the mixing zone of the extruder is connected, through a cooling and temperature control zone, to a die orifice. The hot polymer gel is cooled and then passed through the die orifice into a zone of lower pressure (e.g., normal ambient air atmosphere) where the blowing agent is activated and the polymer gel expands to a lower density, cellular mass. As the foamed extrusion forms, it is conducted away 20 from the die and allowed to cool and harden.

In practice, the temperature of the feed zone is maintained at 180° ± 20°C, the temperature of the melting, metering, and mixing zones is maintained at 210° ± 20°C, and the temperature in the cooling and temperature control zone is maintained at 120° ± 20°C. The temperature of the polymer gel as it expands through the die orifice is preferably just above the temperature at which solid polymer would crystallize out 25 of the gel and will vary depending upon the particular ethylenic or styrenic polymer utilized.

The resulting lightly crosslinked polymer foams comprise substantially closed-cell structures and are flexible to bending and shaping. The foams have excellent dimensional stability and high compressive strengths and heat distortion temperatures.

As is conventional, finely divided solid materials such as talc, calcium silicate, zinc stearate, and the like 30 can advantageously be incorporated with the polymer gel prior to expansion. Such finely divided materials aid in controlling the size of the cells and may be employed in amounts up to five percent by weight of the polymer. Numerous fillers, pigments, lubricants, and the like well known in the art can also be incorporated as desired. Antioxidants may be added to retard or suppress the crosslinking reaction. In such an instance where antioxidant is present in or added to the polymer gel, an additional amount of crosslinking agent may 35 be required to achieve the desired degree of crosslinking.

The specific working examples that follow are intended to illustrate the invention but are not to be taken as limiting the scope thereof as claimed. In the examples, parts and percentages are by weight unless otherwise specified or required by the context.

40 Example I

The apparatus used in this example is a 31,75 mm (1-1/4") screw type extruder having two additional zones for mixing and cooling at the end of usual sequential zones for feeding, melting and metering. An opening for blowing agent injection is provided on the extruder barrel between the metering and mixing 45 zones. A small syringe-type pump is connected to the blowing agent stream for additive injections. At the end of cooling zone, there is attached a die orifice having an opening of rectangular shape. The height of the opening, called die gap hereinafter, is adjustable while its width is fixed at 6.35 mm (0.25").

A granular styrene/acrylic copolymer (1% acrylic acid, 200,000 M.W.) was uniformly mixed with about 0.2 pph talcum powder and 0.2 pph barium stearate. The mixture was fed into the extruder at an essentially 50 uniform rate of about 4.54 kg (10 pounds) per hour. The blowing agent used was a 70/30 by weight mixture of dichlorodifluoromethane (duPont's FC-12®) and ethanol, which was injected into the extruder at a uniform predetermined rate. The crosslinking agent used in this example is hexamethoxymethylmelamine (HMMM) (CYMEL 303® made by American Cyanamid Co.). A predetermined amount of crosslinking agent was injected in the blowing agent stream in Test Nos. 2 through 5 as shown in Table B. The extruder zones 55 were maintained at 160,200 and 200°C for feeding, melting, metering and mixing zone, respectively. The temperature of cooling zone was maintained to achieve a uniform gel temperature of 145°C throughout the tests. When all temperatures reached a steady state, the effect of die gap on foam appearance and line pressures was determined.

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After about a week, the foams were tested for high temperature resistance. Foam slugs of a about 6.35 mm (0.25") thickness are sliced out of foam strands and subjected to hot air of predetermined temperature for one hour. Percent retention of foam volume after the test was recorded as an indication of collapse resistance.

As shown in Table B, HMMM at a level up to 0.9 pph has a minimal effect on the pressures and, accordingly, the threshold die gap for prefoaming does not vary with the HMMM level. At 0.76 mm (0.030") die gap, good foams are made independent of HMMM level. The results clearly substantiate that alcohol, indeed, delays the crosslinking reaction in the foam extrusion line.

TABLE D

TEST NO.	BA LEVEL (1)	HMMM LEVEL (2)	DIE GAP (3)	DIE PRES. (4)	EXTR. PRES. (5)	FOAM THICK. (6)	FOAM WIDTH (7)	FOAM DENS. (8)	CELL SIZE (9)	PREFOAMING (7)(10)	COLLAPSE RESISTANCE (11)				
											100	110	115	120	125°C
1	1.45	--	0.746(0.030)	3.14(660)	4.43(660)	12.7(0.50)	28.5(1.12)	17.68(1.74)	0.44	verge	136	182	227	32	15
2	1.44	0.2	(0.030)3.34(480)	4.43(700)	11.94(0.47)	31.0(1.22)	33.6(2.10)	0.49	verge	140	182	232	39	19	
3	1.46	0.5	(0.030)3.34(520)	5.35(750)	13.46(0.53)	30.7(1.21)	29.6(1.85)	0.42	verge	143	184	229	46	21	
4	1.47	0.7	(0.030)3.34(520)	5.34(760)	12.7(0.50)	32.26(1.27)	29.6(1.86)	0.31	verge	145	184	232	47	23	
5	1.47	0.9	(0.030)3.54(510)	5.84(740)	12.7(0.50)	34.0(1.34)	29.0(1.86)	0.45	no	145	185	226	50	25	

(1) parts of 70/30 by weight mixture of dichlorodifluoromethane and ethanol mixed in per hundred parts of polymer

(2) parts of hexamethoxymethylmelamine (CYMEL 303 made by American Cyanamid) mixed in per hundred parts of polymer

(3) the gap of die opening in mm (inches)

(4) pressure at the die in MPa (pounds per square inch)

(5) pressure at the extruder discharge in MPa (pounds per square inch)

(6) thickness of foam body in mm (inches)

(7) width of foam body in mm (inches)

(8) density of foam body in kg/m³ (pounds per cubic foot) determined after 6 months aging

(10) condition of foam strand coming out of the die: blips = blow holes, verge = verge of prefoaming, no = no foaming

(11) foam volume as a percentage of the initial after aging in an oven of given temperature for one hour

Example II

In the tests in this example, there were used the same apparatus, its operating procedure, polymer, blowing agent and cell size control agent as used in Example I. Additionally, there were added one pph FR651A and 0.03 pph magnesium oxide. FR651A is a trade name flame retardant manufactured by Dow Chemical Company. The extruder zones were set down a little to prevent decomposition of the flame

retardant: 140, 170 and 176°C for feeding, melting, metering and mixing zone, respectively. The gel temperature was varied slightly as presented in Table C.

As shown in Table C, HMMM has little impact on die pressure and extruder discharge pressure manifesting the inhibiting effect of alcohol. The most remarkable thing with the formulations is improvement
5 in collapse resistance. The threshold temperature for collapse, as defined by the maximum temperature at which foam retains at least 90% of its original volume, increases with the HMMM level. It increases from 120 to 125°C for formulations containing 0.5 to 0.9 pph, 140°C for one containing 1.0 pph and 160°C for one with 2.0 pph HMMM. It appears that the flame retardant additive catalyzes the crosslinking reaction and that the HMMM needs to exceed about 1.0 pph to impart significant thermo-collapse resistance to a foam
10 product. However, it is possible to lower the required level by adding the more potent external catalyst such a paratoluenesulfonic acid.

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TABLE C

TEST NO.	UA LEVEL (1)	HPMA LEVEL (2)	FOAMING GEL TEMP. (12)	DIE GAP (3)	DIE PRES. (4)	EXTR. PRES. (5)	FOAM THICK. (6)	FOAM WIDTH (7)	FOAM DENS. (8)	FOAM CELL SIZE (9)	PREFOAMING (10)	COLLAPSE RESISTANCE (11) 110	120	125	130	140	150	160	170°C
1	1.14	--	135	1.02 (0.040)	3.15 (450)	4.97 (710)	14.73 (0.58)	32.51 (1.28)	40.53 (2.53)	0.90	no	221	207	45	34	21	ND	ND	ND
2	1.49	0.5	144	0.76 (0.030)	3.79 (540)	5.2 (750)	13.21 (0.52)	33.02 (1.30)	32.84 (2.05)	0.46	verge	177	212	99	80	36	ND	ND	ND
3	1.41	0.7	144	0.76 (0.030)	3.57 (510)	5.04 (720)	12.96 (0.51)	31.24 (1.23)	31.88 (1.99)	0.29	no	179	225	105	74	29	ND	ND	ND
4	1.48	0.9	144	0.76 (0.030)	3.36 (480)	4.90 (700)	11.18 (0.44)	30.73 (1.21)	30.76 (1.92)	0.28	verge	167	201	95	66	28	ND	ND	ND
5	1.31	1.0	135	1.02 (0.040)	3.08 (440)	4.26 (680)	16.00 (0.63)	32.51 (1.28)	32.36 (2.02)	0.56	verge	202	303	295	189	103	63	46	26
6	1.31	2.0	135	1.02 (0.040)	3.04 (435)	5.04 (720)	13.72 (0.54)	34.51 (1.28)	36.68 (2.29)	0.35	verge	202	267	289	292	241	158	118	89

ND = not determined

(1) parts of 70/30 by weight mixture of dichlorodifluoromethane and ethanol mixed in per hundred parts of polymer
(2) through (11) = the same as in Table B
(12) temperature of foaming gel in degrees centigrade

Example III

The apparatus and its operating procedure used in this example was the same as in Example II. An ethylene/acrylic acid copolymer having 6.5% acrylic acid and 2.0 melt index was evaluated in this work.

HMMM (American Cyanamid's CYMEL 303®) was used as the crosslinking agent and talcum powder as the cell size control agent. Three different types of blowing agents, as shown in Table D, were employed to observe the effect of alcohol. The zones of extruder were set at 150, 180 and 180°C for feeding, melting, metering and mixing zone, respectively. The gel temperature was maintained at 100, 104 and 102°C for FC-12, FC-12/EtOH and FC-114/MeOH blowing agent, respectively.

Table D sets forth the test results. With the absence of alcohol in Test No. 2, 0.2 pph HMMM is sufficient to overcrosslink the polymer in the foam extrusion line. Melt fracture of the foam strand accompanied with a sharp increase in line pressure plagues the test. Test Nos. 4 and 6 demonstrate the reaction-delaying effect of alcohol. At a HMMM level as high as 1.5 pph, good foams are made without a large increase in pressures and flow instability. The crosslinked foams show improvement of collapse resistance. The foam made in Test No. 6 contained 42% insoluble gel after an extraction test in boiling xylene for 24 hours and the polymer was no longer flowable.

TABLE D

TEST NO.	BLOWING AGENT TYPE LEVEL (12)	(pph) (1)	TALC LEVEL (13)	HMAH LEVEL (2)	DIE GAP (3)	DIE PRES. (4)	EXTR. PRES. (5)	FOAM THICK. (6)	FOAM WIDTH (7)	FOAM DENS. (8)	CELL SIZE (9)	PREFOAMING (?) (10)	COLLAPSE RESISTANCE 95	100	105	110	115°C (11)
1	FC-12	20.1	0.3	--	4.57 (0.18)	3.01 (430)	8.47 (1210)	36.56 (1.44)	38.35 (1.51)	25.79 (1.61)	1.01	verge	96	87	31	30	ND
2	FC-12	21.6	0.3	0.2	4.57 (0.18)	4.20 (600)	2.04 (1720)	36.07 (1.42)	40.64 (1.60)	34.92 (2.18)	1.62	melt fract	88	00	26	13	ND
3	FC-12/EtOH:80/20	18.8	0.4	--	3.30 (0.13)	2.66 (380)	6.23 (890)	31.24 (1.23)	36.83 (1.45)	31.56 (1.97)	1.25	no	100	97	56	40	29
4	FC-12/EtOH:80/20	10.8	0.4	0.7	3.30 (0.13)	3.04 (435)	6.86 (900)	31.5e (1.24)	41.66 (1.64)	30.28 (1.89)	1.25	no	99	98	85	71	62
5	FC-114/MeOH:90/10	24.3	0.6	--	2.54 (0.10)	2.83 (405)	7.28 (1040)	22.60 (0.89)	34.54 (1.36)	25.79 (1.61)	1.01	no	95	89	17	13	ND
6	FC-114/MeOH:90/10	24.4	0.6	1.5	2.54 (0.10)	3.18 (455)	8.43 (1210)	20.06 (0.79)	34.29 (1.35)	28.19 (1.76)	1.08	no	93	82	49	31	41

ND - not determined

(1) parts of blowing agent mixed in per hundred parts of polymer
(2) through (11) - the same as in Table B
(12) FC-12 - dichlorodifluoromethane, FC-114 - dichlorotetrafluoroethane, EtOH - ethanol, MeOH - methanol
(13) parts of talcum powder mixed in per hundred parts of polymer

Example IV

The apparatus used in this example is the same as that used in Example I.

The polymer used in this example was a terpolymer of styrene, acrylonitrile and hydroxy ethylacrylate
5 (75% styrene, 25% acrylonitrile and 0.22% HEA) having about 157,000 molecular weight. The polymer was fed into the extruder at an essentially uniform rate of about 4.54 kg (10 pounds) per hour. A 70/30 by weight mixture of fluorocarbon 12 (FC-12) and isopropyl alcohol (i-PrOH) was premixed and injected into the extruder at a uniform rate of about 0.73 kg (1.6 pounds) per hour. For tests incorporating titanium isopropoxide, a predetermined amount of the crosslinking agent was premixed with the blowing agent so
10 that the aimed level could he achieved in the final composition. The extruder zones were maintained at about 170, 190 and 200° C for feeding, melting, metering, and mixing zone, respectively. The temperature of the cooling zone was adjusted so that the gel would reach a uniform temperature for optimum foam expansion.

Good quality foams were achieved from the polymer with or without the addition of titanium isopropox-
15 ide. As set forth in Table E, the line pressures went up slightly but the increases were probably due to the slight drop in the foaming gel temperature. The increase of the die pressure within the tolerable range is desirable in the extrusion process since the enhanced die pressure permits us to achieve the larger foam cross-section without incurring prefoaming. A control formulation, i.e., without crosslinking agent, Test 1, resulted in prefoaming at the given condition while those containing titanium isopropoxide crosslinking agent
20 produced good foams free from prefoaming. The foam strands had oval cross-section of about 17.78 - 25.4 mm (0.7 - 1.0 inches) in the smaller diameter and 25.4 - 35.56 mm (1.0 - 1.4") in the larger diameter. As shown in Table E, the foams had densities of about 38.45 - 40.5 kg m^{-3} (2.4 - 2.5 pcf) and expansion ratios of about 24-27. The expansion ratio is defined by the ratio of specific foam volume to polymer volume.

The distinct benefit of titanium isopropoxide addition was seen during secondary expansions of the
25 foam products with hot air or atmospheric steam. As shown in Table E, titanium isopropoxide makes the foams expand significantly better in both air and steam. Its effect is most pronounced in steam expansion. The foam made with 0.34 pph titanium isopropoxide expands to a size almost twice as large as the control. The highly expanded foam products were light and resilient with their thin flexible cells walls. The details of expansion procedures are described below.

30 For both expansion tests, foams aged for about a week were employed. For hot air expansion tests, foam strands were sliced to about 19.05 mm (3/4" in) length. The specimens were subjected to hot air in a convective oven maintained at a predetermined constant temperature for one hour. The weight and volume of a foam specimen before and after the expansion test were determined and the expansion ratios were calculated. Among five different temperatures tried ranging from 100 to 120° C, 110° C provided the best
35 expansions for all compositions and thus the results are reported in Table E.

For steam expansion tests, foams were sliced to about 6.35 mm (1/4") thick slugs and subjected to atmospheric steam for various periods ranging from five seconds to two hours. Foam specimens having undergone expansions exceeding about 60 expansion ratio shriveled when taken out of the steam but substantially recovered in about two days. The expansion ratios reported in Table E are based on the
40 steady state volume determined in five days. All foams attained the maximum expansions during 7 to 15 min. exposure to steam which are set forth in Table E. The longer exposure to steam resulted in gradual deterioration of expansion.

All foams were found soluble in methyl ethyl ketone (MEK). Approximately 0.2 g of each foam was dissolved in about 25 ml of MEK. The result indicates that there may develop some build-up of molecular
45 weight but a high level of crosslinking does not occur with the polymer at the given level of crosslinking agent. Probably, the titanate plasticizes the polymer and extends the polymer chain slightly resulting in the favorable steam expansions.

50

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TABLE E

TEST NO.	BA LEVEL (pph) [1]	TiT LEVEL (pph) [2]	FOAMING TEMP. (C°) [3]	DIE PRES. (psi) [4]	EXTRUD. PRES. (psi) [5]	FOAM DENSITY (pcf) [6]	INITIAL EXPANSION RATIO [7]	EXPANSION IN HOT AIR (Expansion Ratio) [8]			EXPANSION IN STEAM (Expansion Ratio) [9]					
								100°C	110°C	120°C	10 sec	1 min	10 min	15 min	max (10)	max time (min) (11)
1	15.6	--	134 (490)	3.73 (490)	17.20 (600)	38.4 (2.40)	27	33	30	6.3	49	76	90	35	101	15
2	16.0	0.2	133 (300)	4.0 (300)	13.03 (1730)	37.6 (2.35)	24	36	41	6.4	54	75	126	19	150	7
3	16.0	0.34	132 (600)	4.2 (600)	13.39 (1900)	38.4 (2.40)	25	39	49	0.2	57	101	109	28	102	7

All tests were run at the following conditions:

Nucleator type and level : 0.1 pph Best 0.1 pph talc
Die gap : 0.110"

[1] Parts of a 70/30 mixture of fluorocarbon 12/isopropyl alcohol mixed in a per hundred parts of polymer
[2] Parts of titanium isopropoxide mixed in per hundred parts of polymer
[3] Temperature of foaming gel in degrees centigrade
[4] Pressure at the die in kPa (pounds per square inch)
[5] Pressure at the extruder discharge in kPa (pounds per square inch)
[6] Density in kg m⁻³ (pounds per cubic foot) of foam body aged for about a week
[7] Expansion ratio of foam body determined prior to secondary expansions which were conducted in about a week
[8] Expansion ratio of foam body after exposure to hot air at the specified temperature for one hour
[9] Expansion ratio of foam body after exposure to atmospheric steam for the specified time and aging for 5 days
[10] Maximum expansion ratio of foam body after expansion in steam
[11] Steam exposure time corresponding to the maximum expansion ratio

Claims

1. A process for preparing lightly crosslinked olefin or styrenic polymer foamed articles having a closed-cell structure, characterized by the steps of:

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a) providing an olefin or styrene polymer material, selected from the group consisting of:

(1) olefin copolymers;

(2) styrene copolymers, vinyltoluene polymers, styrene/acrylonitrile/hydroxy ethylacrylate terpolymers and mixtures thereof; and

(3) a polymer of styrene having hydroxyl, carboxylic acid and carbonyl functional groups, optionally mixed with anyone of the foregoing styrenic polymers;

b) admixing said olefin or styrene polymer material with (1) a blowing agent, (2) a crosslinking agent selected from the group consisting of silane, azido silane, titanate and amino compounds which upon reaction with said olefin or styrene polymer material reversibly releases alcohol, and (3) additionally admixing a sufficient amount of alcohol to control the degree of crosslinking of said olefin or styrene polymer material in the admixture which is thereby formed, and

c) extruding said admixture and activating said blowing agent in such a manner as to expand said olefin or styrene polymer material to a cellular structure and at the same time dissipate said alcohol, whereby foaming and crosslinking of said olefin or styrene polymer material concurrently takes place.

2. The process of claim 1 wherein said crosslinking agent is an organofunctional alkoxy silane selected from the group consisting of gamma-glycidoxypropyltrimethoxy silane, gamma-methacryloxypropyltrimethoxy silane, vinyltrimethoxy silane, vinyltriethoxy silane, N-(2-aminoethyl)-3-aminopropyltrimethoxy silane, N-β-(N-vinyl benzyl amino) ethylaminopropyltrimethoxy silane, methyltrimethoxy silane, and gamma-aminopropyl trimethoxy silane.

3. The process of claim 1 wherein said crosslinking agent is an azido silane of the formula R R'SiY$_2$ in which R represents an azido functional radical attached to silicon through a silicon to carbon bond and composed of carbon, hydrogen, sulfur, nitrogen, or oxygen, each Y represents a hydrolyzable organic radical, and R' represents a monovalent hydrocarbon radical or a hydrolyzable organic radical.

4. The process of claim 3 wherein said crosslinking agent is selected from the group consisting of 2-(trimethoxysilyl)ethyl phenyl sulfonyl azide and (triethoxy silyl) hexyl sulfonyl azide.

5. The process of claim 1 wherein said crosslinking agent is a titanate having a general formula Ti(OR)$_4$ where R is C$_1$ to C$_{18}$ alkyl or having a formula (RO)$_m$ - Ti(O-X-R^2-Y)$_n$, wherein R is alkyl, X is carboxyl, R^2 is alkyl, Y is a reactive double bond or amino, and m and n are integers which total 4.

6. The process of claim 5 wherein said crosslinking agent is selected from the group consisting of titanium isopropoxide, and tetramethyl titanate.

7. The process of claim 1 wherein said crosslinking agent is selected from the group consisting of hexamethoxymethylmelamine and alkylated glycoluril-formaldehyde resins.

8. The process of claim 1 wherein said olefin or styrene polymer material is selected from the group consisting of styrene/acrylic acid copolymers, ethylene/acrylic acid copolymers, styrene/acrylonitrile/hydroxy ethylacrylate terpolymers, and mixtures thereof.

9. The process of claim 8 wherein said alcohol is an aliphatic alcohol selected from the group consisting of methanol, ethanol, n-propanol, i-propanol, and butanol.

10. The process of claim 9 wherein said blowing agent is selected from the group consisting of dichlorodifluoromethane, trichloromonofluoromethane, dichlorotetrafluoroethane and mixtures thereof.

11. The process of claim 1 wherein said olefin or styrene polymer material is selected from the group consisting of styrene/acrylic acid copolymer and ethylene/acrylic acid copolymers and said crosslinking agent is hexamethoxymethylmelamine.

12. The process of claim 1 wherein said olefin or styrene polymer is a styrene/acrylonitrile/hydroxy ethylacrylate terpolymer and said crosslinking agent is selected from the group consisting of titanium isopropoxide, and tetramethyl titanate.

Patentansprüche

1. Verfahren zur Herstellung von geschäumten Gegenständen aus wenig vernetztem Olefinpolymerem oder styrolartigem Polymerem, die geschlossene Zellstruktur besitzen, gekennzeichnet durch die
5   Stufen:
    a) Bereitstellung eines Olefin- oder Styrolpolymermaterials, ausgewählt aus der Gruppe bestehend aus:
        (1) Olefincopolymeren;
        (2) Styrolcopolymeren, Vinyltoluolpolymeren, Styrol/Acrylnitril/Hydroxyethylacrylat-terpolymeren
10   und Mischungen hiervon; und
        (3) einem Polymeren von Styrol, das funktionelle Hydroxyl-, Carboxyl- und Carbonylgruppen besitzt, gegebenenfalls vermischt mit irgendeinem der vorangegangen styrolartigen Polymeren;
    b) Zusammenmischen dieses Olefin- oder Styrolpolymermaterials mit (1) einem Blähmittel, (2) einem Vernetzungsmittel, ausgewählt aus der aus Silan-, Azidosilan-, Titanat- und Aminoverbindun-
15   gen bestehenden Gruppe, welche bei Reaktion mit diesem Olefin- oder Styrolpolymermaterial reversibel Alkohol freisetzen, und (3) zusätzliches Zumischen einer ausreichenden Menge von Alkohol zur Steuerung des Vernetzungsausmaßes dieses Olefin- oder Styrolpolymermaterials in der Zusammenmischung, die hierdurch gebildet wird, und
    c) Extrudieren dieser Zusammenmischung und Aktivieren dieses Blähmittels in einer solchen Weise,
20   daß dieses Olefin- oder Styrolpolymermaterial zu einer Zellstruktur geschäumt wird und gleichzeitig diesen Alkohol abgibt, wodurch Schäumen und Vernetzen dieses Olefin- oder Styrolpolymermaterials gleichlaufend stattfinden.

2. Verfahren nach Anspruch 1, worin dieses Vernetzungsmittel ein organofunktionelles Alkoxysilan ist,
25   ausgewählt aus der aus gamma-Glycidoxypropyltrimethoxysilan, gamma-Methacryloxypropyltrimethoxysilan, Vinyltrimethoxysilan, Vinyltriethoxysilan, N-(2-Aminoethyl)-3-aminopropyltrimethoxysilan, N-β-(N-Vinylbenzylamino)-ethylaminopropyltrimethoxysilan, Methyltrimethoxysilan und gamma-Aminopropyltrimethoxysilan bestehenden Gruppe.

30 3. Verfahren nach Anspruch 1, worin dieses Vernetzungsmittel ein Azidosilan der Formel $RR'SiY_2$ ist, worin R ein an Silizium über eine Silizium-Kohlenstoffbindung gebundener und aus Kohlenstoff, Wasserstoff, Schwefel, Stickstoff oder Sauerstoff bestehender, azidofunktioneller Rest ist, jedes y einen hydrolisierbaren organischen Rest darstellt, und R' einen einwertigen Kohlenwasserstoffrest oder einen hydrolisierbaren organischen Rest darstellt.
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4. Verfahren nach Anspruch 3, worin dieses Vernetzungsmittel aus der aus 2-(Trimethoxysilyl)-ethylphenylsulfonylazid und (Triethoxysilyl)-hexylsulfonylazid bestehenden Gruppe ausgewählt wird.

5. Verfahren nach Anspruch 1, worin dieses Vernetzungsmittel ein Titanat ist, das eine allgemeinen
40   Formel $Ti(OR)_4$ hat, worin R C_1 bis C_{18}-Alkyl ist, oder eine Formel $(RO)_m$-$Ti(O$-X-R^2-$Y)_n$ hat, worin R Alkyl ist, X Carboxyl ist, R^2 Alkyl ist, Y eine reaktive Doppelbindung oder Amino ist und m und n ganze Zahlen mit der Summe 4 sind.

6. Verfahren nach Anspruch 5, worin dieses Vernetzungsmittel aus der aus Titanisopropoxid und Tetrame-
45   thyltitanat bestehenden Gruppe ausgwählt wird.

7. Verfahren nach Anspruch 1, worin dieses Vernetzungsmittel aus der aus Hexamethoxymethylmelamin und alkylierten GlycolurilFormaldehydharzen bestehenden Gruppe ausgewählt wird.

50 8. Verfahren nach Anspruch 1, worin dieses Olefin- oder Styrolpolymermaterial aus der aus Styrol/Acrylsäure-copolymeren, Ethylen/Acrylsäure-copolymeren, Styrol/Acrylnitril/Hydroxyethylacrylat-terpolymeren und Mischunghen hiervon bestehenden Gruppe ausgewählt wird.

9. Verfahren nach Anspruch 8, worin dieser Alkohol ein aliphatischer Alkohol, ausgewählt aus der aus
55   Methanol, Ethanol, n-Propanol, i-Propanol und Butanol bestehenden Gruppe, ist.

10. Verfahren nach Anspruch 9, worin dieses Blähmittel aus der aus Dichlordifluormethan, Trichlormonofluormethan, Dichlortetrafluorethan und Mischungen hiervon bestehenden Gruppe ausgewählt wird.

11. Verfahren nach Anspruch 1, worin dieses Olefin- oder Styrolpolymermaterial aus der aus Styrol/Acrylsäure-copolymeren und Ethylen/Acrylsäure-copolymeren bestehenden Gruppe ausgewählt wird.

12. Verfahren nach Anspruch 1, worin dieses Olefin- oder Styrolpolymere ein Styrol/Acrylnitril/Hydroxyethylacrylatterpolymeres ist und dieses Vernetzungsmittel aus der aus Titanisopropoxid und Tetramethyltitanat bestehenden Gruppe ausgewählt wird.

Revendications

1. Procédé pour fabriquer des articles expansés de polymère oléfinique ou styrénique légèrement réticulés ayant une structure de cellule fermée, caractérisé par les étapes consistant:
   (a) à fournir une matière de polymère de styrène ou d'oléfine, choisi dans le groupe formé par :
      (1) des copolymères d'oléfine;
      (2) des copolymères de styrène, des polymères vinyltoluène, des terpolymères styrène/acrylonitrile/acrylate d'hydroxyéthyle et leurs mélanges; et
      (3) un polymère de styrène ayant des groupements fonctionnels carbonyle et acide carboxylique, éventuellement mélangés avec l'un quelconque des polymères styréniques précédents;
   b) à mélanger ladite matière de polymère de styrène ou d'oléfine avec (1) un agent d'expansion, (2) un agent de réticulation choisi dans le groupe formé par les silane, azido silane, titanate et composés aminés qui, en réaction avec ladite matière de polymère de styrène ou d'oléfine, libère de l'alcool de façon réversible, et (3) en plus à mélanger une quantité suffisante d'alcool pour maîtriser le degré de réticulation de ladite matière de polymère de styrène ou d'oléfine dans le mélange ainsi formé, et
   c) à extruder ledit mélange et à activer ledit agent d'expansion de façon à expanser ladite matière de polymère d'oléfine ou de styrène en une structure cellulaire et en même temps à dissiper ledit alcool, l'expansion et la réticulation de ladite matière de polymère de styrène ou d'oléfine ayant ainsi lieu simultanément.

2. Procédé selon la revendication 1, dans lequel ledit agent de réticulation est un alcoxy silane organofonctionnel choisi dans le groupe formé par le gamma-glycidoxypropyltriméthoxy silane, le gamma-méthacryloxypropyltriméthoxy silane, le vinyltriméthoxy silane, le vinyltriéthoxy silane, le N-(2-aminoéthyl)-3-aminopropyltriméthoxy silane, le N-β-(N-vinyl benzyl amino) éthylaminopropyltriméthoxy silane, le métyltriméthoxy silane, et le gamma-aminopropyltriméthoxy silane.

3. Procédé selon la revendication 1, dans lequel ledit agent de réticulation est un azido silane de formule $RR'SiY_2$ dans lequel R représente un radical fonctionnel azido lié à un atome de silicium par une liaison silicium-carbone et est composé de carbone, d'hydrogène, de soufre, d'azote, ou d'oxygène, chaque Y représente un radical organique hydrolysable, et R' représente un radical hydrocarbure monovalent ou un radical organique hydrolysable.

4. Procédé selon la revendication 3, dans lequel ledit agent de réticulation est choisi dans le groupe formé par le 2-triméthoxysilyl)éthylphénylsulfonyl azide et le (triéthoxysilyl)hexylsulfonyl azide.

5. Procédé selon la revendication 1, dans lequel ledit agent de réticulation est un titanate ayant une formule générale $Ti(OR)_4$ dans laquelle R représente un groupement alkyle en C_1 à C_{18} ou ayant pour formule $(RO)_m$-$Ti(O-X-R^2-Y)_n$ dans laquelle R représente un groupement alkyle, X représente un groupement carboxyle, R^2 représente un groupement alkyle, Y représente un groupement amino ou une double liaison réactive, et m et n sont des nombres entiers qui font au total 4.

6. Procédé selon la revendication 5, dans lequel ledit agent de réticulation est choisi dans le groupe formé par l'isopropylate de titane, et le titanate tétraméthyle.

7. Procédé selon la revendication 1, dans lequel ledit agent de réticulation est choisi dans le groupe formé par l'hexaméthoxyméthylmélamine et les résines glycolurilformaldéhyde alkylées.

8. Procédé selon la revendication 1, dans lequel ladite matière de polymère de styrène ou d'oléfine est choisie dans le groupe formé par les copolymères styrène/acide acrylique, les copolymères

éthylène/acide acrylique, les terpolymères styrène/acrylonitrile/acrylate d'hydroxy d'éthyle, et leurs mélanges.

9. Procédé selon la revendication 8, dans lequel ledit alcool est un alcool aliphatique choisi dans le groupe formé par le méthanol, l'éthanol, le n-propanol, l'i-propanol, et le butanol.

10. Procédé selon la revendication 9, dans lequel ledit agent d'expansion est choisi dans le groupe formé par le dichlorodifluorométhane, le trichloromonofluorométhane, le dichlorotétrafluoroéthane et leurs mélanges.

11. Procédé selon la revendication 1, dans lequel ladite matière de polymère de styrène ou d'oléfine est choisie dans le groupe formé par le copolymère styrène/acide acrylique et les copolymères éthylène/acide acrylique et ledit agent de réticulation est l'hexaméthoxyméthylmélamine.

12. Procédé selon la revendication 1, dans lequel ladite matière de polymère de styrène ou d'oléfine est un terpolymère styrène/acrylonitrile/oxylate d'hydroxyéthyle et ledit agent de réticulation est choisi dans le groupe formé par l'isopropylate de titane et le titanate de tétraméthyle.